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Remarks on the calculation of characteristic temperatures of cubic crystals from the elastic constants

By E. TENERZ

Summary

The Debye characteristic temperature θ_D for cubic crystals is calculated from the elastic constant, using the method first introduced by Bhatia and Tauber (1954). These authors expand the mean velocity of the three elastic waves in Kubic Harmonics K_m of which they take only three into account. Extending that method by taking five K_m, of which the fifth is deduced here, a relative simple expression for θ_D is still obtained. It is accurate even for large elastic anistrophy. A numerical comparison with Quimby and Sutton's (1953) method shows a very good agreement in the cases where this method is convenient to use. The numerical work is almost the same for both the methods in these cases, otherwise much less when Kubic Harmonics are used. Values of θ_D for a number of substances and temperatures are calculated. The new calculation of θ_D for KCl at 0° K exhibits good agreement with measurements in the T^3-range. The fifth K_m can be of interest in other calculations.

Introduction

In terms of the phase velocities Debye's characteristic temperature θ_D is given by the well-known formula:

$$\theta_D = \frac{h}{k}\left(\frac{9\,S}{\Delta}\right)^{\frac{1}{3}} I^{-\frac{1}{3}}, \tag{1}$$

where

$$I = \int \sum_i \frac{1}{v_i^3(\theta\,\phi)}\,d\Omega. \tag{2}$$

Here h and k are Planck's and Boltzmann's constants respectively, s denotes the number of atoms in a cell, Δ is the volume of the cell and $v_i(\theta\,\phi)$ are the velocities of the three elastic waves for a direction $(\theta\,\phi)$. The integration in (2) is extended over all directions of propagation.

For a cubic crystal the three velocities, associated with a given propagation vector are, according to the theory of elasticity, found from the roots of the cubic equation:

$$u^3 - u^2 + (1-K^2)\,\Gamma\,u - (1-3\,K^2+2\,K^3)\,\chi = 0 \tag{3}$$

where

$$K = \frac{c_{12} + c_{44}}{c_{11} - c_{44}} \quad \Gamma = (x^2 y^2 + y^2 z^2 + x^2 z^2); \; \chi = x^2 y^2 z^2; \; u_i = \frac{\varrho v_i^2 - c_{44}}{c_{11} - c_{44}}.$$

c_{ik} are the elastic constants, ϱ is the mass density and x, y, z are the direction cosines of the propagation vector referred to the cubic axis.

Calculation of θ_D by expansion of I into Kubic Harmonics

The Kubic Harmonics $K_m(x, y, z)$ were first introduced by von der Lage and Bethe [5]. These functions are linear combinations of spherical harmonics so constructed as to be invariant under the symmetry operations characteristic of a cubic lattice. The problem of constructing them is, firstly, to find combinations of terms of the form $x^p y^q z^t \, (l = p + q + t)$ which fulfil the symmetry relations and, secondly, to combine them so that they are orthogonal to each combination with lower l.

In von der Lage and Bethe's paper only the first four K_m are given.[1] For the purpose of this note K_4 has also been calculated. The expression for the first five Kubic Harmonics used in this calculation are:

$$K_0 = 1; \; K_1 = k_1 (x^4 + y^4 + z^4 - \tfrac{3}{5} r^4); \; K_2 = k_2 (x^2 y^2 z^2 + \tfrac{1}{22} [K_1] r^2 - \tfrac{1}{105} r^6);$$

$$K_3 = k_3 (x^8 + y^8 + z^8 - \tfrac{28}{5} [K_2] r^2 - \tfrac{210}{143} [K_1] r^4 - \tfrac{1}{3} r^8);$$

$$K_4 = k_4 (x^{10} + y^{10} + z^{10} - \tfrac{45}{19} [K_3] r^2 - \tfrac{126}{17} [K_2] r^4 - \tfrac{210}{143} [K_1] r^6 - \tfrac{3}{11} r^{10})$$

where $r^2 = x^2 + y^2 + z^2$ and k_m are the normalization constants. The functions in square brackets are not normalized, i.e. they represent, K_0, K_1/k_1, K_2/k_2 and K_3/k_3.

Expanding the integrand in (2) in Kubic Harmonics we get:

$$I = \int \sum_{m=0}^{\infty} \alpha_m K_m \, d\Omega = 4\pi \alpha_0. \tag{4}$$

An approximate value of α_0 can now be obtained by using a finite number of terms in the expansion, determining the phase velocities for a number of directions equal to the number of terms in the expansion and finally solving for the coefficient α_m. This method, first used by Bhatia and Tauber [1], leads to a relatively simple expression for I, if only the first few terms are taken into account. Bhatia and Tauber, howewer, used only the first three K_m, which seems sufficient for crystals where the factor of anisotropy $[\eta = 2 c_{44}/(c_{11} - c_{12})]$ is not too far from one. In order to calculate θ_D for crystals with large anisotropy we have extended their calculation, taking the first five K_m into account, and we made a comparison for some crystals with the result obtained when only the first three or four K_m are considered.

When five K_m are used $v_i(\theta \phi)$ must be evaluated from (3) for five different directions, for four K_m four directions and for three K_m three directions. If η approaches one, α_0 in (4) becomes independent of the choice of directions and of the number of terms in the expansion, but when η is far from one, α_0 will depend on the number of terms as well on the directions chosen in so far as the number of K_m used is not sufficient. On account of this α_0 has been calculated for different combinations of directions, when three and four K_m are considered. For three K_m five combinations have been used and for four K_m three combinations, which are in Table 1.

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[1] The expression for K_3 contains a misprint.

Table 1. The directions used in the calculation of θ_D.

	Three K_m					Four K_m			Five K_m
	I	II	III	IV	V	VI	VII	VIII	IX
$x\ y\ z$	$\frac{2}{\sqrt{5}}\ \frac{1}{\sqrt{5}}\ 0$	100	$\frac{2}{\sqrt{5}}\ \frac{1}{\sqrt{5}}\ 0$	100	100	100	100	100	100
	$\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0$	$\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0$	$\frac{2}{\sqrt{6}}\ \frac{1}{\sqrt{6}}\ \frac{1}{\sqrt{6}}$	$\frac{2}{\sqrt{5}}\ \frac{1}{\sqrt{5}}\ 0$	$\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0$	$\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0$	$\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0$	$\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0$	$\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\ 0$
	$\frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}$	$\frac{2}{\sqrt{6}}\ \frac{1}{\sqrt{6}}\ \frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}$	$\frac{2}{\sqrt{5}}\ \frac{1}{\sqrt{5}}\ 0$	$\frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}\ \frac{1}{\sqrt{3}}$
						$\frac{2}{\sqrt{5}}\ \frac{1}{\sqrt{5}}\ 0$	$\frac{2}{\sqrt{6}}\ \frac{1}{\sqrt{6}}\ \frac{1}{\sqrt{6}}$	$\frac{2}{\sqrt{6}}\ \frac{1}{\sqrt{6}}\ \frac{1}{\sqrt{6}}$	$\frac{2}{\sqrt{5}}\ \frac{1}{\sqrt{5}}\ 0$
									$\frac{2}{\sqrt{6}}\ \frac{1}{\sqrt{6}}\ \frac{1}{\sqrt{6}}$

For the sake of brevity the expression for I is given only in the case of five K_m.

$$I = \frac{4\pi}{10\,395}\left[\frac{1197}{c_{11}^{3/2}} + \frac{6975}{c_{44}^{3/2}} + \frac{1456}{(c_{44}+\frac{1}{2}\varepsilon)^{3/2}} + \frac{1456}{(c_{11}-\frac{1}{2}\varepsilon)^{3/2}} + \frac{729}{(c_{11}-\frac{2}{3}\varepsilon)^{3/2}} + \right.$$

$$\left. + \frac{1458}{(c_{44}+\frac{1}{3}\varepsilon)^{3/2}} + 3888\left(\frac{1}{c_1^{3/2}} + \frac{1}{c_2^{3/2}} + \frac{1}{c_3^{3/2}}\right) + 3125\left(\frac{1}{c_4^{3/2}} + \frac{1}{c_5^{3/2}}\right)\right] \cdot \varrho^{3/2}. \qquad (5)$$

$$\left.\begin{aligned} c_n &= Z_n\,(c_{11}-c_{44}) + c_{44} \\ Z_n &= \tfrac{1}{3} + 2\sqrt{-\frac{p}{3}}\cos\frac{\alpha + 2(n-1)\pi}{3} \end{aligned}\right\} \quad \text{for } n = 1,\ 2,\ 3$$

$$\left.\begin{matrix} c_4 \\ c_5 \end{matrix}\right\} = c_{11}\,(\tfrac{1}{2} \pm \tfrac{1}{10}\sqrt{9+16\,K^2}) + c_{44}\,(\tfrac{1}{2} \mp \tfrac{1}{10}\sqrt{9+16\,K^2})$$

$$p = -\tfrac{1}{12}(1 + 3\,K^2)$$

$$q = -\tfrac{1}{108}(1 + 3\,K^2 + 4\,K^3)$$

$$r = \sqrt{-\left(\frac{p}{3}\right)^3}\,; \quad \cos\alpha = -\frac{q}{2r}$$

$$\varepsilon = c_{11} - c_{12} - 2c_{44}.$$

Table 2 contains the values of θ_D obtained by this method.

Table 2. The results for θ_D.

	$3K_m$						$4K_m$			$5K_m$
	η	I	II	III	IV	V	VI	VII	VIII	IX
Na at 80° K	8.2	166	137	160	159	128	155	140	143	146
Na at 290° K	7.0	145	123	141	141	116	138	126	129	131
K ,, ,, ,,	6.3	100	86	98	98	81	96	88	90	91
Cu ,, ,, ,,	3.2	341	326	334	338	316	336.2	328.5	330.6	331.9
Au ,, ,, ,,	2.9	158	155	158	161	151	160.0	156.7	157.6	158.2
Ag ,, ,, ,,	2.9	217	209	213	216	204	214.6	210.5	211.5	212.3
Al ,, ,, ,,	1.2	407	407	407	407	407	407.2	407.2	407.2	407.2
NaCl ,, ,, ,,	0.72	303	302	302	303	302	302.7	302.7	302.7	302.7
NaCl at 0° K	0.56	322	321	318	321	319	321.2	321.7	321.6	321.5
KCl at 280° K	0.36	224	224	215	224	219	223.3	225.8	225.1	224.6
KCl at 0° K	0.29	230	230	216	230	222	228.9	233.1	232.0	231.2

The elastic constants are taken from Hearmon [2] except those of NaCl, which are taken from Overtone and Swim [6]. They are all measured at room temperature except those of Na, KCl and NaCl. For Na the elastic constants at 80° K and 290° K have been used, for KCl and for NaCl those at 280° and 290° K respectively have been used as well as those extrapolated to 0° K, for NaCl by Overtone and Swim and for KCl by Durand. In Table 2 one can see that combination II in Table 1 gives the best result, when only three K_m are used. When four K_m are used, the results are more stabilized, and thus the result for five K_m should be rather reliable. From Table 2 it is clear that the use of only three K_m is a good approximation for small anisotropy.

The method of Hopf and Lechner and related methods

The expression (2) can be written as follows:

$$I = 4\pi\left[\frac{\varrho}{(c_{11}-c_{44})}\right]^{3/2} \int_0^{4\pi} \sum_i \frac{1}{(C+u_i)^{3/2}}\,\frac{d\Omega}{4\pi} \tag{6}$$

where

$$C = \frac{c_{44}}{c_{11}-c_{44}}.$$

From this Hopf and Lechner [3] computed the mean Debye characteristic temperature by approximating the integrand in (6) by means of a polynomial of fifth degree. They evaluated the coefficients in the polynomial with Lagrange's method of interpolation for $0 \leq u \leq 1$. After that they only had to calculate $\sum_{i=1}^{3} u_i^n$ $(n = 1 \ldots 5)$ from the coefficients in (3). This method has recently been improved by Quimby and Sutton [7]. These authors also used a polynomial of fifth degree but chosen so as to be exact or nearly exact at the points where the distribution functions of the roots have their maxima. In a later paper [9] Sutton has computed a correction term to (6) and has given this as a function of K and C on a diagram. He has considered the range where $C > 0.25$ and where $-0.85 < (1-K)/2C \leq 0$ or $0 \leq (1-K)/2 \leq 0.5$. This range covers many cubic crystals except, for example, Na, K and KCl. Outside the considered range the approximation with a fifth degree polynomial is not so good and, therefore, this method is then difficult to use.

Schröder and v. Hagenow [8] have written Quimby and Sutton's formula as

$$\omega_D = 2\pi \left\{\frac{3s}{4\pi\Delta}\right\}^{\frac{1}{3}} \left\{\frac{c_{11} - c_{44}}{\varrho}\right\}^{\frac{1}{2}} J(C, K) \tag{7}$$

where

$$\omega_D = \frac{2\pi k}{h} \theta_D.$$

They have evaluated J for different values of C and K in the region where $0 \leq C \leq 2.8$ and $0 \leq K \leq 4.5$. The values obtained for J are written in a diagram. When C and K are known, J can easily be found from the diagram, and θ_D can be computed from (7). The accuracy is, however, only 2 %. The considered range contains several crystals but for example Na lies outside, when Hearmon's data for the elastic constants are used.

In our investigation the correction term to Quimby and Sutton's formula has been computed by expanding in K_m the difference between the integrand in (6) and the fifth degree polynomial. This has been done by means of three K_m, and θ_D was calculated for Na and KCl. The results were 146° for Na (i.e. the same as with formula (5)) and 232.0° for KCl at 0° K.

In order to compare the method of Quimby and Sutton with formula (5) θ_D has been calculated for Au with exactly the same constants. The results were the same for the two methods; $\theta_D = 158.2°$.

For KCl at 0°K the value found for θ_D is in good agreement with that found by experimental measurements of C_v below 2° K. Keesom and Pearlman [4] found $\theta_D = 233 \pm 3°$ K. They calculated θ_D from the T^3-law, which must give a very good approximation in this region.

Formula (5) can be used for every cubic crystal but the convergence is, of course, better the closer η is to unity. The error introduced by this method is, however, insignificant in view of the uncertainty in the experimental determination of the elastic constants, even when η is rather far from unity.

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Institute of Mechanics and Mathematical Physics, University of Uppsala.

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